Arabian Journal of Chemistry (2014) 7, 261–266

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Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Fluorescence quenching of naphthols by Cu^{2+} in micelles

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Received 17 September 2010; accepted 25 October 2010
Available online 3 November 2010

KEYWORDS

Naphthol;
Fluorescence;
Micelle;
Dynamic quenching;
Static quenching;
Excited state lifetime

Abstract Effect of the micelles of anionic, cationic and non-ionic surfactants on the fluorescence quenching of 1- and 2-naphthols has been studied in the presence of copper ion. The excited state lifetime, dynamic and static quenching constants for these systems have been determined. Fluorescence quenching in water and SDS micelle is due to the collision of the fluorophore with the quencher with a small static component. The negatively charged naphtholate ions in the excited state are quenched with significantly higher rates than the neutral naphthol molecules, which are located further inside the mesophase. CTAB micelle is less effective than the SDS micelle for fluorescence quenching. The effect of CTAB on water-assisted excited-state deprotonation has been investigated in the presence of $ZnSO_4$. For TX-100 micelle there is negligible quenching even at higher concentration of the quencher.

1. Introduction

Fluorescence quenching has often been employed as a powerful tool to obtain information on the microstructure and dynamics of the complex aqueous media such as micelles, reversed micelles, and microemulsions. (Almgren and Swarup, 1982; Almgren, 1992; Gehlen and de Schryver, 1993; Panda et al., 1999). It has also been used as a convenient method to characterize the immediate environment of a fluorophore (Ganesh et al., 1982; Rodgers et al., 1978). If water contains a suitable quantity of the surfactant, micelles are formed and the fluorophore gets solubilized by inclusion inside them (Panda et al., 1999; Panda and Mishra, 2002). Naphthols have been known to be excellent probes for the microheterogeneous environments (Mishra et al., 2001); the excited-state deprotonation of 2-naphthol has been suitably used for the determination of the critical micelle concentration (Collins et al., 1999). Both 1-naphthol (1ROH) and 2-naphthol (2ROH) are extremely weak acids in the ground state (pK_as of 1ROH and 2ROH are 9.39 and 9.49, respectively) (Albert and Serjent, 1984; Harris and Selinger, 1980; Ellis, 1966; Lee et al., 1986). Being photon-initiated acids, they show excited state proton transfer (ESPT) at neutral pH (pK_a^*s of 1ROH and 2ROH are 0.4 and 2.8, respectively) (Mandal et al., 1998; Panda et al., 1995, 1998). Copper ion, a physiologically important heavy metal ion, has been known to be a very good quencher of naphthol fluorescence (Panda et al., 1995). In the present work, we have studied

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Peer review under responsibility of King Saud University.

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http://dx.doi.org/10.1016/j.arabjc.2010.10.028

the fluorescence quenching of 1- and 2-naphthols in the anionic, cationic and non-ionic micelles. The following surfactants have been used: (i) sodium dodecyl sulphate (SDS), an anionic surfactant with cmc 8 mM, (ii) cetyltrimethylammonium bromide (CTAB), a cationic surfactant with cmc 0.92 mM, and (iii) Triton X-100, a neutral surfactant with the cmc 0.26 mM.

2. Experimental

1-Naphthol and 2-naphthol, obtained from Sisco-Chem, were purified by subliming after crystallization from alcohol. Copper sulphate (Sigma) was crystallized from water. Triple distilled water was used throughout the study. Freshly prepared solutions were used for all the experiments. Sodium dodecyl sulphate (Sigma) was crystallized from ethyl alcohol. Cetyltrimethylammonium bromide (Sisco-Chem) was crystallized from methanol. TX-100 (Sigma) was used as received. The surfactant concentrations in the solutions were 20 times of their critical micelle concentration.

Absorption and fluorescence spectra were recorded by Hitachi 220A UV–Vis spectrophotometer and Hitachi F-4500 spectrofluorimeter, respectively. Lifetime measurements were carried out using the Horiba-Jobin Yvon IBH single photon counting fluorimeter. The concentrations of the naphthols were 1×10^{-4} M (0.05% methanol) and those of the quenchers were varied in the range 0–0.1 M. The fluorescence intensities of naphthols were monitored at various concentrations of Cu^{2+} at 25 °C.

3. Results and discussion

3.1. Absorption and emission spectra

Both the naphthols behave differently on excitation. 1ROH, on excitation at 290 nm in water, dissociates completely exhibiting an emission peak at 464 nm for $1RO^{-}$* only. However, 2ROH, when excited at 330 nm, shows the emission peaks at 353 nm and 411 nm for neutral (2ROH*) and anionic ($2RO^{-}$*) forms, respectively. The dissociation of both the naphthols is suppressed in the presence of SDS and TX-100, the suppression of dissociation being less in TX-100 micelle as compared to the SDS micelle. Naphthol molecule tries to go inside the micelle because of its nonpolar nature and thus less number of ROH is available at the interface for dissociation. In CTAB micelle, the emission spectra of naphthols are similar to those in water. Here, the dissociation is facilitated due to the specific Coulombic attractive interaction of RO^{-}* with the positively charged nitrogen of CTAB at the interface showing a remarkable intensity enhancement for the anionic peak. The emission spectra of 1- and 2-naphthols in aqueous medium and in different micelles are given in Fig. 1 and the emission wavelengths are compiled in Table 1. For the anionic form of 1-naphthol, a blue shift of 12 nm in the emission spectrum was observed for SDS micelle, which is still more in the CTAB and TX-100 micelles. This indicates a more non-polar environment for $1RO^{-}$* in micelles than water. For 2-naphthol, a bathochromic shift of 3–4 nm in the emission spectra is observed.

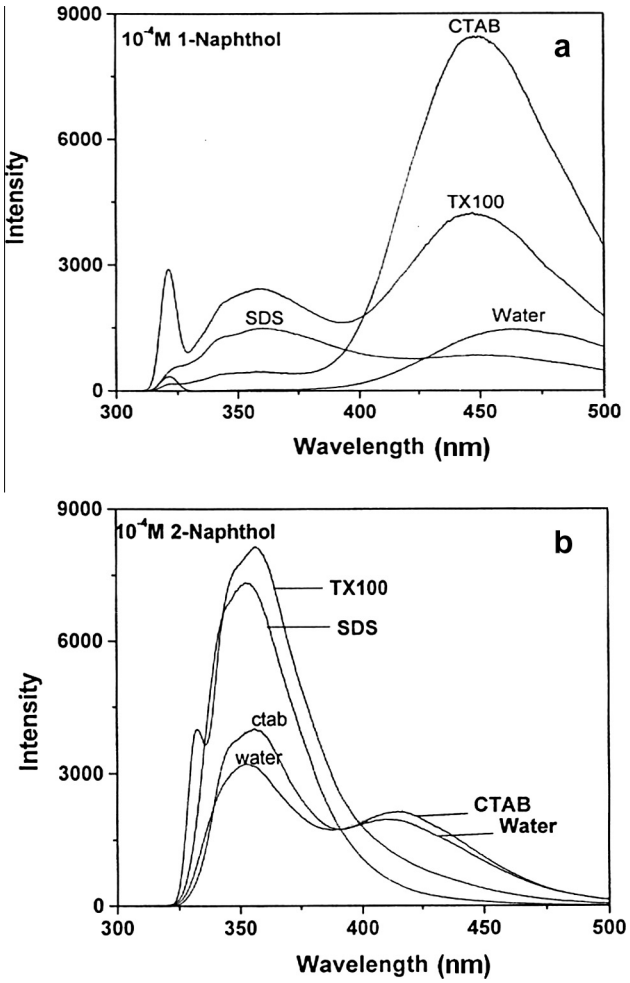

Figure 1 Emission spectra of 1-naphthol (a) and 2-naphthol (b) in water and micelles (indicated).

3.2. Fluorescence behaviour of naphthols in presence of Cu^{2+}

3.2.1. $1RO^{-}$*, 2ROH* and $2RO^{-}$* in aqueous medium

1-Naphthol on excitation dissociates completely in aqueous medium and, therefore, it is not possible to determine the quenching parameters of 1ROH*. For the other species, upon addition of Cu^{2+}, an instantaneous decrease of the fluorescence intensity is observed and the intensity decreases as the concentration of Cu^{2+} is increased. Usually, in the case of collisional quenching (Panda et al., 1995), the Stern–Volmer (SV) plot, *i.e.*, the plot of the ratio of fluorescence intensities in the absence and presence of quencher (I_o/I) against the quencher concentration [Q], is a straight line with an intercept 1 and slope as K_{SV}, the Stern–Volmer quenching constant. In the present study, the Stern–Volmer equation is obeyed by the species $1RO^{-}$* and 2ROH*, but $2RO^{-}$* shows an upward deviation from linearity (Fig. 2). This indicates that quenching is purely dynamic in the first two cases, but for $2RO^{-}$*, quenching is not purely collisional and some other factor is also responsible for quenching. In order to explain the non-linearity in the SV plot, the extended SV equation can be represented as (Behera and Mishra, 1993; Behera et al., 1995)

Table 1 Emission wavelength (λ_{em}), excited state lifetime (τ_0), dynamic quenching constant (K_D) and static quenching constant (K_S) values of 1-naphthol and 2-naphthol in different environments.

Fluorophore	λ_{em} (nm)				τ_0 (ns)				K_D (mol^{-1} dm^3)			K_S (mol^{-1} dm^3)		
	Water	SDS	CTAB	TX-100	Water	SDS	CTAB	TX-100	Water	SDS	CTAB	Water	SDS	CTAB
1ROH*	–	361	355	360	0.50	1.84	0.50	3.08	–	152.22	–	–	–	–
$1RO^-$*	464	452	449	447	8.07	8.40	16.04	16.2	96.77	295.64	–	–	7.16	–
2ROH*	353	354	357	357	4.72	8.28	3.77	8.64	38.59	386.03	–	–	–	–
$2RO^-$*	411	–	415	–	9.13	9.36	–	–	118.63	–	–	6.04	–	–

Error limits of K_D and K_S are ±3%.

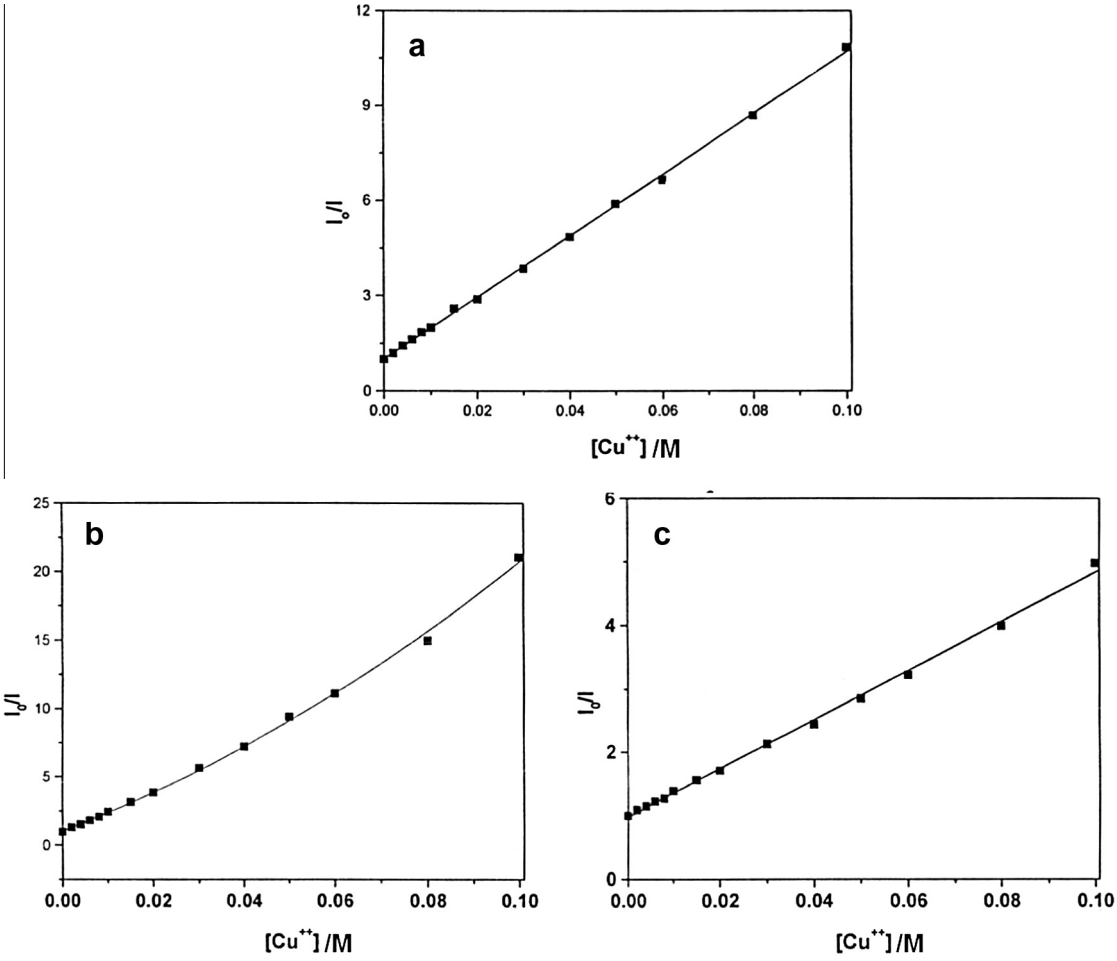

Figure 2 Stern–Volmer plots of $1RO^-$* (a), $2RO^-$* (b) and 2ROH* (c) in water.

$$I_o/I = 1 + (K_D + K_S)\,[Q] + K_D K_S\,[Q]^2 = 1 + K_1\,[Q] + K_2\,[Q]^2 \quad (1)$$

$$\text{or,}\quad (I_0/I - 1)/[Q] = K_1 + K_2\,[Q] \quad (2)$$

In Eq. (1), K_D and K_S stand for dynamic and static quenching, respectively.

The values of K_D and K_S have been calculated by Eq. (1) and are given in Table 1. The K_D values are in the order $2RO^-$* > $1RO^-$* > 2ROH* (Table 1). The effect observed is a combined effect of the dynamic and static components. It is seen that the values of K_S are very less as compared to K_D, which explains the lack of spectral change on the addition of copper ion. The larger value of K_D could be due to a more stable encounter complex (ROH*·Cu^{2+}).

3.2.2. 1ROH and 2ROH*, $1RO^-$* and $2RO^-$* in micelles*

The fluorophore and quencher can be solubilized in the micelle and remain in the same or different microenvironments. The absorption spectra of naphthols in the presence and absence of the quencher show no observable change in spectral shape and maxima. For both the fluorophores, no unusual fluorescence spectral changes and spectral shift have been observed in SDS micelle in the presence of Cu^{2+} other than diminishing the fluorescence intensity. This indicates that the electronic transition of the fluorophore is not perturbed by the micellar

environment. The probable localization site of copper ion is the interface due to the Cu^{2+}–Na^{+} exchange. $1RO^{-}$* is repelled by the negatively charged interface of SDS and thus resides in the bulk water. For $1RO^{-}$* there is a positive deviation in the SV plot (Fig. 3), because of the presence of a static component in addition with dynamic quenching process. For neutral species, the plots are linear ($r > 0.99$) indicating the presence of dynamic quenching. The K_D values are in the order 2ROH* > $1RO^{-}$* > 1ROH* (Table 1). Higher K_D value for $1RO^{-}$* than for 1ROH* is due to electrostatic effect. Mallick et al. (2006) have studied the quenching of fluorescence of 3-acetyl-4-oxo-6,7-dihydro-12H-indolo-[2,3-a]-quinolizine by Cu^{2+} ion as a function of the SDS concentration. They have also rationalized the enhancement of the fluorescence intensity as a function of SDS concentration by considering two competing processes: electrostatic interaction between the anionic SDS micellar surface and the positive metal ion (Cu^{2+}), and lesser accessibility of the probe molecules towards the metal ions within the micellar environment.

In TX-100 micelle the highly hydrated head group surfaces (provided by the POE groups) increase the thickness of the interface. The state of water in the POE domain could be such that POE-water clusters are formed via hydrogen bonds. Because of the thickness of the layer (the so-called mantle), the probe is almost entirely confined to it and copper ion does not come near the naphthol molecules decreasing the encounter probability of the probe with the quencher; thus there is no quenching even at higher concentrations of the quencher. Molecules entrapped within the micelle are also protected from quenching.

Because of the positively charged interface of the CTAB micelle, copper ion resides in the bulk water away from the interface, 1ROH* resides in the micellar pocket and $1RO^{-}$* near the positively charged interface. Thus only few copper ions are accessible to both 1ROH* and $1RO^{-}$* for quenching; the SV plots show leveling effect after a particular concentration of copper ion (Fig. 4). Such a leveling effect is observed only when there are two populations of the fluorophores, out of which only one is accessible to the quencher. 1ROH* and $1RO^{-}$*, present near the interface, are accessible to the quencher whereas 1ROH* in the micellar pocket and $1RO^{-}$* in the bulk water do not come in contact of the quencher which causes saturation in the SV plot after a particular concentration. Addition of salts screens the electrostatic head-group repulsion between amphiphiles within the micelle, allowing the surface area per micelle to be reduced. Because of this 2-naphthol molecule might be pulled towards the interface with the availability of more water for a better dissociation. For 2ROH in CTAB micelle, the dissociation goes on increasing till the concentration of the copper ion reaches 0.02 M, after

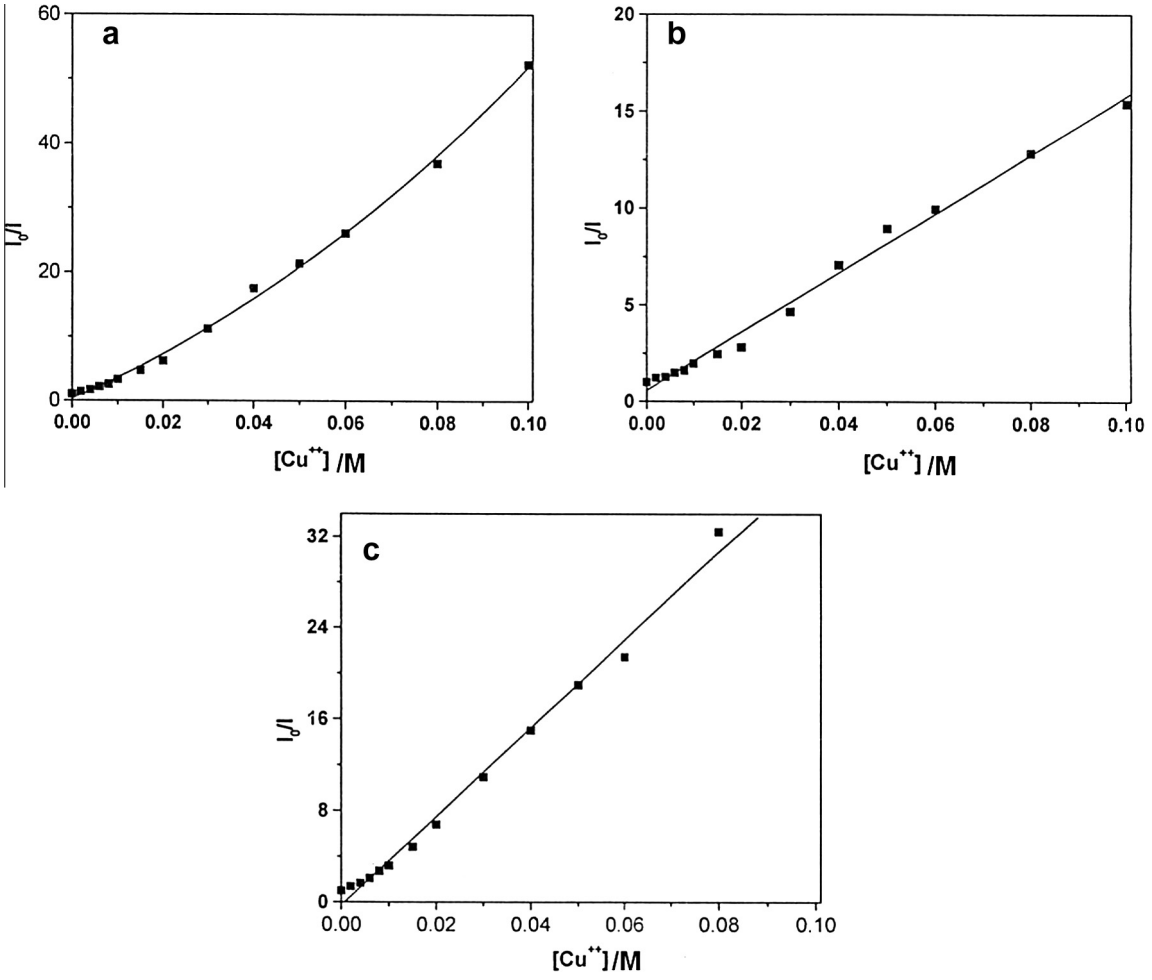

Figure 3 Stern–Volmer plots of $1RO^{-}$* (a), 1ROH* (b) and 2ROH* (c) in SDS micelles.

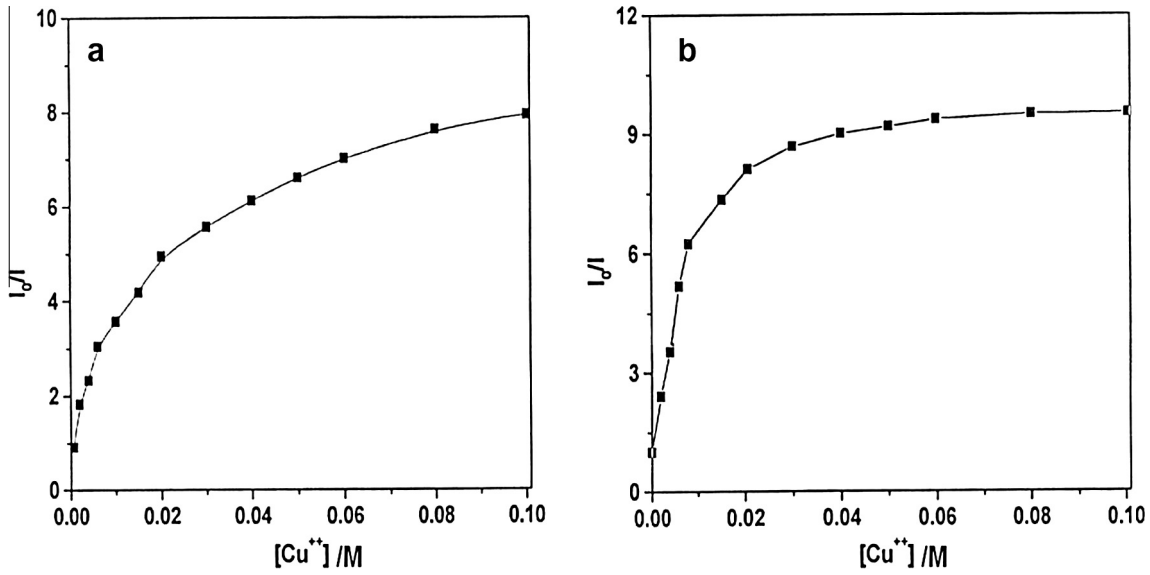

Figure 4 Stern–Volmer plots of $1RO^-$* (a) and 1ROH* (b) in CTAB micelles.

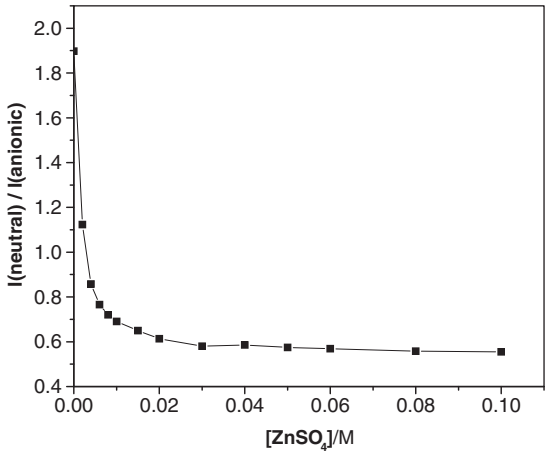

Figure 5 Dissociation of 2-naphthol in CTAB micelles in the presence of $ZnSO_4$.

which dissociation stops and quenching starts. To confirm whether there is any quenching process in addition to the increase in dissociation of 2ROH, $ZnSO_4$, a non-quencher, was tried. As $ZnSO_4$ does not quench the species, only the increase in dissociation of 2ROH* is observed till the concentration of the salt becomes 0.02 M (Fig. 5). Thus, when the salt concentration becomes equal to the concentration of CTAB (18.4×10^{-3} M) in the micellar solution, dissociation of 2ROH* stops. As both the dissociation and quenching processes are occurring simultaneously, it is difficult to suggest a particular quenching process for 2ROH-$CuSO_4$ system.

4. Conclusions

Both the naphthols, in their excited singlet state, become stronger acid in the presence of CTAB than in water whereas in SDS micelle they become weaker acid. The present work has clarified the differential quenching behaviour of Cu^{2+} in different micelles. Emission from both the neutral and anionic forms of naphthols gets quenched by copper ion. Cu^{2+} is an efficient quencher of naphthol fluorescence for anionic micelles because its positive charge allows entry into the micelle, whereas in cationic micelle it is repelled and is less effective. Quenching in water and SDS micelle is due to the collision of the fluorophores with the quencher with a small static component. The negatively charged 1-RO^-* and 2-RO^-* are quenched with significantly higher rates than the neutral naphthol molecules, which were located further inside the mesophase. Excited state deprotonation of 2-naphthol becomes enhanced in CTAB micelle in the presence of $CuSO_4$ or $ZnSO_4$. In CTAB micelle, addition of salts screens the electrostatic head-group repulsion between amphiphiles within the micelle, allowing the surface area per micelle to be reduced. Here, 2-naphthol molecule might be pulled towards the interface with the availability of more water for a better dissociation.

Acknowledgements

We are thankful to Prof. A.K. Mishra, Department of Chemistry, IIT, Madras, for helpful discussion and for allowing to measure the fluorescence lifetime. Financial assistance by the Department of Science and Technology, Government of India, is gratefully acknowledged.

References

Albert, A., Serjent, E.P., 1984. The Determination of Ionization Constants. Chapman and Hall, London, pp. 145.
Almgren, M., 1992. Adv. Colloid Interf. Sci. 41, 9.
Almgren, M., Swarup, S., 1982. J. Phys. Chem. 86, 4212.
Behera, P.K., Mishra, A.K., 1993. J. Photochem. Photobiol. A: Chem. 71, 115.
Behera, P.K., Mukherjee, T., Mishra, A.K., 1995. J. Lumin. 65, 137.
Collins, D., Kadelski, S., Lonardo, R., Peterson, B., Reddy, C., Marzzacco, C.J., Halpern, A.M., Nassiri, F., 1999. Recent Res. Develop. Photochem. Photobiol. 3, 77.

Ellis, D.W., 1966. J. Chem. Educ. 43, 259.
Ganesh, K.N., Mitra, P., Balasubramanian, D., 1982. J. Phys. Chem. 86, 4291.
Gehlen, M.H., de Schryver, F.C., 1993. Chem. Rev. 93, 199.
Harris, C.M., Selinger, B.K., 1980. J. Phys. Chem. 84, 891.
Lee, J., Robinson, G.W., Webb, S.P., Philips, L.A., Clark, J.H., 1986. J. Am. Chem. Soc. 108, 6538.
Mallick, A., Mandal, M.C., Haldar, B., Chakrabarty, A., Das, P., Chattopadhyaya, N., 2006. J. Am. Chem. Soc. 128, 3126.
Mandal, D., Pal, S.K., Bhattacharyya, K., 1998. J. Phys. Chem. A 102, 9710.
Mishra, A.K., 2001. In: Ramamurthy, V., Schanze, K.S. (Eds.), Understanding and Manipulating Excited State Processes, Molecular and Supramolecular Photochemistry Series, vol. 8. Marcel Dekker, Inc., New York, p. 577 (Chapter 10).
Panda, M., Mishra, A.K., 2002. J. Photosc. 9, 75.
Panda, M., Behera, P.K., Mishra, B.K., Behera, G.B., 1995. J. Photochem. Photobiol. A 90, 69.
Panda, M., Behera, P.K., Mishra, B.K., Behera, G.B., 1998. J. Photochem. Photobiol. A 113, 73.
Panda, M., Behera, P.K., Mishra, B.K., Behera, G.B., 1999. Adv. Colloid Interf. Sci. 82, 1.
Rodgers, M.A.J., Da Silva, E., Wheeler, M.F., 1978. Chem. Phys. Lett. 53, 165.